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STUDY OF CORROSION PRODUCTS IN THE SEATTLE WATER DEPARTMENT TOLT DISTRIBUTION SYSTEM

Robert A. Dangel

National Environmental Research Center
Gig Harbor, Washington

May 1975

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Samples from the Seattle Water Department's Tolt distribution system were analyzed for chemical and bacteriological parameters. Changes from the raw water quality were observed, particularly in trace metal concentrations and other parameters related to corrosion. Distribution mains were found to be adequately protected from corrosion by cement and bituminous linings whereas service lines and household plumbing were actively corroded. Metals in the µg/l concentration range were determined by a flameless atomic absorption technique.

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By

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Water Supply Research Laboratory

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NATIONAL ENVIRONMENTAL RESEARCH CENTER
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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment—air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This study examined the changes in potable water quality in a large urban distribution system. The data supports the conclusion that corrosion control is needed to reduce the pick-up of metals by the water.

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Director
National Environmental
Research Center, Cincinnati

ABSTRACT

Samples from the Seattle Water Department's Tolt distribution system were analyzed for chemical and bacteriological parameters. Changes from the raw water quality were observed, particularly in trace metal concentrations and other parameters related to corrosion. Distribution mains were found to be adequately protected from corrosion by cement and bituminous linings whereas service lines and household plumbing were actively corroded.

Metals in the µg/l concentration range were determined by a flameless atomic absorption technique.

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CONCLUSIONS

When the iron, copper, zinc, lead, and cadmium means for the standing samples are compared with the raw water values (Table 6), the corrosiveness of Tolt water is confirmed. Comparison of the running and standing means indicates that most of the metal pick-up is occurring in the service lines and plumbing inside buildings. This occurs despite the fact the residence time in the distribution system is about 1 week and only overnight in the building plumbing. The data also indicate that the distribution mains are adequately protected by their cement and bituminous linings.

A combination of an alkalinity increase of 1 mg/l (as $CaCO_3$) and a turbidity increase of 0.1 FTU from running to standing samples is indicative of corrosion. In the absence of a metal analysis, this could be used as a qualitative index.

Laboratory analysis of corrosion products correlates well with the materials in contact with the water. Buried pipe could be identified by comparing the influent and effluent metal concentrations.

Tolt water passing through asbestos-cement pipe exhibited radical changes in pH, alkalinity, calcium, and conductivity, which increased with longer exposure to the pipe. Although the samples are within the limits of the P.H.S. Standards, they are indicative of rapid pipe wear. As the cement binder is dissolved, asbestos fibers may possibly be leaching from the pipe walls. The water quality changes in asbestos-cement pipe are in marked contrast to the inertness of cement-lined cast iron pipe in contact with Tolt water.

Standing samples were collected without regard to the number of hours the water was exposed to the building plumbing. Further study is needed to determine whether a standard residence period is necessary to ensure reproducible data.

Bacteriological samples were part of the standing group. They contained corrosion products which might have inhibited bacterial growth. Further work should include running samples to determine whether the organisms detected in the standard plate count grow primarily in the distribution system or in the building plumbing.

The data and conclusions presented in this report should help in further study of both the Tolt and Cedar distribution systems. Also, they will provide baseline data for future evaluation of corrosion control chemicals in the Tolt distribution system.

INTRODUCTION

Seattle obtains its water from two surface sources, the Cedar River and the south fork of the Tolt River. The watersheds are in mountainous areas closed to public access.

Before collection, the runoff has a short contact time with the soil. The hardness, alkalinity, salinity, and trace metal content of these waters is remarkably low and the dissolved oxygen content approaches saturation. The resulting water is an excellent solvent and exhibits aggressive corrosion tendencies.

Treatment consists of screening, gaseous chlorination, fluoridation (25% H_2SiF_6), and rechlorination at distribution reservoir outlets. The addition of these chemicals to the recommended levels causes an alkalinity decrease of 2.5 to 3.5 mg/l as $CaCo_3$, and lowers the pH 0.2 to 0.4 units in Cedar water and 0.4 to 0.8 units in Tolt water. Besides transforming bicarbonate alkalinity to carbonic acid, the hypochlorous acid and hypochlorite ions may increase the water's activity on metal because of their oxidizing power.

Seattle, recognizing the corrosive tendencies of its water, requested technical assistance from the U. S. Environmental Protection Agency to determine the severity and location of the corrosion problem. The availability of the facilities at the Northwest Water Supply Research Laboratory made the study possible.

SAMPLING PROCEDURE

The Tolt distribution system was chosen for this study because it accounts for a larger per capita percentage of the red water complaints than does the Cedar system. The Tolt's lower pH, alkalinity, and hardness also make it the more corrosive of the two supplies. At the time of the study, the Tolt supplied about one third of the water used in Seattle.

The water mains in the city were predominately cement and bituminous lined and were assumed to be adequately protected from the corrosive waters. Service connections and residential plumbing were not similarly protected and were assumed to be the source of the corrosion products. To test this hypothesis, two types of samples were collected in the early morning hours from the source, transmission mains, distribution system, and residences. Standing samples collected from the first water to run out of the faucet represented water in contact with the household piping for at least one night. Running samples collected after a 30-second bleeding of the lines represented water from the mains.

The standing sample consisted of a quart of water to be used for determining trace metals, another quart for wet chemistry, and then smaller amounts for dissolved oxygen and bacteriological analyses. The water was then allowed to run before additional quarts were taken for trace metals and wet chemistry analyses. Concentrated nitric acid (1.5 ml) was added to the trace metal samples as a preservative.

Bacteriological testing was not the major thrust of this study, and one set of tests per location was believed to be adequate.

Samples were collected in the early morning hours by members of the Seattle Water Department. Numbers 1 through 4 and 6 through 12 were collected on October 12, 1972. Numbers 5 and 13 through 34 were collected on October 26, 1972. Analysis of both sets was completed on December 8, 1972.

ANALYTICAL METHODS

The chemical constituents chosen for analysis were those directly related to corrosion or corrosion products. In addition, bacteriological and fluoride determinations were performed. In the preliminary work, chromium, nickel, and cobalt were found to be below 10 µg/l and, therefore, were not included in the analysis sequence. Residual chlorine concentration was not measured because it fluctuates too widely to be correlated with corrosion data.

The procedures selected for the analytical methods were:

Temperature was measured at the time the sample was collected.

Dissolved oxygen was determined by the Azide modification of the Winkler method in Standard Methods. (1) Analyses were performed by the Seattle Water Department.

Conductivity was determined with an A. R. Thomas Model 15B1 Serfass conductivity bridge and a Beckman 0.1 factor conductivity cell.

Color rarely matched the color standards of the Hellige Aqua Tester. Where possible, color densities were measured. Otherwise, samples appearing different from the distilled water blank, when compared in matched 50-ml Nessler tubes, were recorded as having color.

Fluoride was determined with a Corning fluoride ion electrode on a Corning Model 101 meter. All samples were mixed 1:1 with TISAB buffer. Commercial standards were used.

pH was determined with a glass electrode and silver/silver chloride reference on a Corning Model 101 meter. The low buffering capacity of the water made the determination difficult. A sample at pH 5.4 would drift to pH 6.0 in 10 to 30 minutes while being stirred in an open beaker. This drift indicated a loss of carbon dioxide.

Total alkalinity was determined by the potentiometric method, titrating to pH 4.5 and 4.2 with 0.0020N HCl. A reagent one-tenth the recommended strength was needed because of the low alkalinities.

Turbidities were determined with a Hach 2100A unit. Calibration was obtained from standards provided with the instrument at 0.61 and 10 Formazine turbidity units. The values were not corrected for the background light scattering of the blank which was about 0.04 FTU.

Chloride was determined with a Corning chloride ion electrode and a Corning Model 101 meter. Standards were prepared by diluting commercial products.

Bacteriological samples were analyzed by Standard Methods techniques. The plate count is reported as organisms/ml, incubated at 35°C. Coliform and pseudomonas are reported as organisms/100 ml.

Metals were determined by flame atomic absorption and graphite furnace atomic absorption on a Perkin Elmer 303, with a strip chart recorder. Standards were obtained by diluting commercial products. Values obtained in percent absorption were converted to absorbance and then to concentration from a parabolic calibration curve by computer. Cadmium, lead, manganese, and the lower values for copper and iron were obtained by the furnace technique, with the Perkin-Elmer HGA 2000 Heated Graphite Atomizer. Calcium, magnesium, zinc, high copper, and high iron values were obtained by the flame technique. The detection limits for zinc and cadmium were 0.015 mg/l and 0.4 µg/l respectively. A lanthanum chloride solution was added to the calcium and magnesium samples and standards to eliminate chemical interferences.

Trace metal standards from the Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, Cincinnati, were analyzed in conjunction with this study to check the accuracy of the determinations. Six concentrates were used to spike deionized water and also a composite of Seattle tap water which was made by combining a number of the standing samples. Both sets were analyzed by flame and furnace atomic absorption. The deionized water contained no background metals, and the values obtained were solely from the spike. The results for the spike in the tap water samples were obtained by subtracting the metal concentration of the tap water from the total of the tap water and the spike. For these waters, the accuracy of the furnace technique is excellent, even at the 1 µg/l level (as shown in Table 1). A separate report describing the technique and operating parameters for the graphite furnace can be found in the appendix.

RESULTS

The data are presented in Tables 2 through 5 and in Table 6 are the means and maximums. Values are reported as mg/l or µg/l, depending on the range of concentrations. "S" is for standing and "R" is for running samples.

Standing samples were not collected from sample stations numbers 2 through 4, 7 through 12, 16, 18, and 28. These locations were taps directly from distribution mains and other places that did not have significant volumes of water in long contact with the piping materials.

TABLE 1

RECOVERY OF DISSOLVED METALS ADDED TO DISTILLED WATER AND A COMPOSITE SEATTLE TAP WATER BY CONVENTIONAL AND HEATED GRAPHITE ATOMIZER ATOMIC ABSORPTION[a]

Metal	Known[b]	Flame[c]		Furnace[d]		Known	Flame		Furnace	
		DW[e]	TW[f]	DW	TW		DW	TW	DW	TW
	SAMPLE 1						SAMPLE 5			
Cd	71	100	100	72	75	1.4	N[h]	N	1.4	1.8
Cr	370	370	370	408	408	7.4	bdl	bdl	8	7
Cu	302	270	140	301	339	7.5	40	30	7	7
Fe	840	800	860	880	833[g]	24	bdl	bdl	22	23
Pb	367	480	480	295	301	37	bdl	bdl	36	38
Zn	281	297	267			7.0	12	3		
	SAMPLE 2						SAMPLE 6			
Cd	14	N	N	13	14	2.8	N	N	2.5	2.9
Cr	74	90	90	77	74	15	bdl	bdl	15	15
Cu	60	60	-30	56	41	12	bdl	bdl	11	12
Fe	350	220	280	336	339	10	bdl	bdl	9	1
Pb	101	bdl[i]	bdl	90	86	25	bdl	bdl	25	24
Zn	70	57	44			11	14	7		
	SAMPLE 3						BACKGROUND LEVEL IN COMPOSITE TAP WATER			
Cd	18	N	N	17	18		bdl		0.8	
Cr	93	90	90	100	95		bdl		0.7	
Cu	75	80	-10	78	59		470		550	
Fe	438	420	430	422	449		250		272	
Pb	84	bdl	bdl	75	74		bdl		4.9	
Zn	70	77	59				606			
	SAMPLE 4									
Cd	78	100	100	79	84					
Cr	407	420	420	475	475					
Cu	332	300	170	364	383					
Fe	700	670	730	682	709[g]					
Pb	334	310	310	275	270					
Zn	310	328	300							

a All values in µg/l
b Amount added to DW and TW samples
c Conventional atomic absorption
d Heated graphite atomizer atomic absorption (HGA 2000)
e Recovery of metal added to deionized water
f Recovery of metal added to composite Seattle tap water in the presence of the background levels shown in the Table
g Total value above range of HGA 2000. Flame value substitued in the subtraction.
h Signal too noisy to read
i Below detection limit

TABLE 2 - WET CHEMISTRY DATA

Sample Number	Sample Site	Temperature, °C		D.O., mg/l		Conductivity, μmho, 20°C		Turbidity, FTU		pH		Alkalinity, mg/l $CaCO_3$		Chloride, mg/l	
		R[a]	S[b]	R	S	R	S	R	S	R	S	R	S	R	S
1	Hoyt, 10602 NE 137 Pl, Kirkland	12	18	10.5	9.2	22	24	0.48	0.58	5.3	5.6	2.3	4.2	1.6	1.6
2	Tolt Regulating Basin, Before Treatment	12		10.6		18		0.45		5.4		~4		1.0	
3	Tolt Treatment Bldg, After Cl_2,F-	13		10.7		20		0.43		5.5		~2		1.7	
4	Tolt Pipeline Air Valve #9	13		10.5		20		0.72		5.3		0.9		1.6	
5	Seeklander, 7015 14th NW	14	15	10.0	9.0	21	21	0.41	0.45	6.0	5.8	1.1	2.0	2.6	2.3
6	Duvall Shops	13		10.3	10.0	23	23	0.50	0.62	5.2	5.4	2.7	3.3	1.7	1.7
7	Tolt pipeline, Air valve #21	13		10.5		21		1.8		5.4		~2		1.6	
8	" " Air valve #24	13		10.4		21		2.4		5.3		0.9		1.7	
9	" " LK Forest Pk Res.	13		10.4		20		0.45		5.8		2.4		1.6	
10	" " NE 195 & 35 NE	13		10.4		20		0.45		5.1		0.9		1.7	
11	Foy Pump Station	13		10.5		21		0.47		5.3		1.3		1.6	
12	North Gate Pump Station	13		10.5		20		0.43		5.3		1.4		1.6	
13	Jessup, 625 N. 180th	12	12	10.7	5.6	22	29	0.45	1.8	5.9	5.8	2.6	7.2	2.3	2.4
14	Duvall, Fire Station	12	16	8.7	8.9	42	42	1.0	0.94	8.9	9.1	~14	~14	2.6	2.4
15	Bulter, Duvall	11	10	10.6	9.6	25	28	0.47	13	5.9	5.8	4.1	6.6	2.4	2.3
16	N. City Pump Station	12		10.8		18		0.48		6.0		2.8		2.3	
17	Richmond Beach Library	14	14	10.1	7.1	23	28	0.48	0.60	5.9	6.2	3.5	6.8	2.5	2.2
18	" " Sample Station	14		9.9		23		1.2		5.9		2.5		2.2	
19	Taylor, 19527 Stone Ave. N	12	13	8.3		24	27	0.90	1.3	6.3	6.7	4.9	6.3	2.5	2.2
20	Courchene, 1622 N 51st	15	16	10.4	7.0	21	21	0.47	0.88	5.7	5.9	1.1	2.2	2.4	2.4
21	Lehman, 116 N 78th	13	18	10.5	5.2	22	24	0.50	3.3	5.7	6.0	2.2	4.3	2.5	2.6
22	Brehan, 8526 19th Ave. NW	14	17	10.5	9.7	23	23	0.44	0.50	5.8	5.8	2.4	3.6	2.6	2.6
23	Moore, 935 N 128th	13.5	17	10.8	9.6	21	24	0.54	28	5.6	6.0	1.1	2.1	2.2	2.2
24	Larson, 10041 14 Ave. NW	13	10	10.3	9.5	22	26	0.48	0.84	5.7	6.0	1.6	5.4	2.7	2.5
25	Buckingham, 12733 8th NW	13	17	10.2	7.8	22	33	0.46	6.3	5.8	6.1	1.9	~6	2.6	4.6
26	Thompson, 8751 16th NW	13	13.5	10.3	10.2	22	23	0.58	0.83	5.9	5.8	2.5	2.7	2.4	2.6
27	Schwind, 8351 22nd NW	13.5	19.5	10.0	7.6	21	27	0.52	1.3	5.8	6.1	1.7	5.6	2.3	2.4
28	Bitter LK Res. Sample Station	12		10.4		23		0.49		5.8		2.2		2.9	
29	Vining, 9523 Evanston Ave. N	12.5	13.5	10.5	4.7	22	23	0.52	3.8	5.8	5.9	2.5	3.4	2.1	2.4
30	Scholz, 11727 Corliss Ave. N	12.5	12.5	10.7	10.2	21	22	0.46	0.50	5.7	5.8	2.0	2.0	2.2	2.3
31	Fanson, 12336 3rd Ave. NE	13	22	10.3	4.9	22	26	0.50	2.8	5.7	5.7	2.0	4.5	2.4	2.6
32	Bringhurst, 843 NE 78 NE	13	13.5	10.7	9.9	21	22	0.46	0.67	5.6	5.7	1.7	3.0	2.1	2.1
33	Broswick, 537 NE 81st	13	14	10.6	10.3	21	22	0.46	0.55	5.7	5.6	1.6	1.4	2.1	2.2
34	Philbrick, 11702 22nd Ave. NE	12	14	10.6	6.4	20	22	0.48	3.0	6.0	5.7	2.3	2.5	2.2	2.3
	High	14	19.5	10.8	10.3	42	42	2.4	28	8.9	9.1	14	14	2.9	4.6
	Low	11	10	8.3	4.7	18	21	0.41	0.45	5.1	5.4	0.9	1.4	1.0	1.6
	Mean	13	15	10.3	8.2	22	25	0.63	3.3	5.8	6.1	2.5	4.5	2.1	2.4
	% Relative Std Deviation			5.0	23.4	19	19	67	188			89	61	21	23
	Std Deviation			0.51	1.9	4.2	4.8	0.42	6.2			2.2	2.8	0.44	0.55

a Running Sample
b Standing Sample

TABLE 1 - METALS DATA

Sample Number	Cu, mg/l		Mn, µg/l		Fe, mg/l		Pb, µg/l		Zn, mg/l		Cd, µg/l		Mg, mg/l		Ca, mg/l	
	R	S	R	S	R	S	R	S	R	S	R	S	R	S	R	S
1	0.10	1.02	10	10	0.16	0.32	2	9	0.05	0.16	*	*	0.31	0.31	2.71	2.66
2	0.002		18		0.17		1		*		*		0.33		2.07	
3	0.24		16		0.15		1		*		*		0.33		2.06	
4	0.005		16		0.27		17		*		*		0.32		2.13	
5	0.069	0.10	14	19	0.21	0.48	4	4	0.05	0.31	*	0.7	0.32	0.33	2.66	2.54
6	1.67	1.92	16	19	0.17	0.53	2	4	*	0.39	*	0.4	0.32	0.37	2.06	2.11
7	0.006		45		1.1		22		*		*	*	0.32		2.13	
8	0.008		33		0.75		21		*		*	*	0.31		2.13	
9	0.003		9		0.16		1		*		*	*	0.29		2.22	
10	0.097		9		0.14		1		*		*	*	0.29		2.10	
11	0.049		9		0.17		1		0.03		*	*	0.30		2.11	
12	0.010		7		0.15		2		0.05		*	*	0.30		2.21	
13	0.035	0.14	10	19	0.21	1.6	4	36	0.28	3.65	*	1.4	0.28	0.29	2.87	2.64
14	0.007	0.21	11	6	0.26	0.25	1	13	0.79	0.09	*	*	0.08	0.08	7.27	7.34
15	0.030	0.028	11	26	0.18	1.5	2	12	0.07	2.07	*	0.4	0.18	0.21	3.94	3.82
16	0.029		13		0.19		3		*		*		0.28		2.22	
17	0.12	1.09	7	5	0.19	0.19	5	26	*	0.06	*	*	0.29	0.26	3.03	2.13
18	0.019		29		0.35		2		*		*		0.30		3.01	
19	0.042	0.038	23	47	1.2	0.70	3	12	1.73	3.42	*	0.6	0.29	0.29	2.68	2.74
20	0.082	0.24	14	22	0.26	1.1	3	17	0.08	0.81	*	0.8	0.30	0.32	2.58	2.50
21	0.043	0.091	15	43	0.30	2.0	12	16	0.27	2.24	0.8	4.9	0.30	0.31	2.43	2.41
22	0.15	0.20	7	12	0.19	1.2	3	11	0.08	0.79	*	0.6	0.26	0.26	3.03	2.88
23	0.072	2.05	10	79	0.24	>70	2	170	0.11	32.6	*	14	0.29	0.27	2.53	2.20
24	0.061	0.12	7	11	0.17	0.68	11	71	0.08	2.12	*	0.8	0.26	0.27	2.95	2.88
25	0.018	0.87	6	20	0.15	0.37	2	51	0.15	5.46	*	0.5	0.26	0.38	2.88	3.81
26	0.021	0.080	7	15	0.27	0.91	2	13	0.03	1.05	*	25	0.38	0.24	3.22	2.89
27	0.022	0.037	14	19	0.26	0.48	2	17	0.14	2.78	*	2.1	0.31	0.41	2.48	3.24
28	0.053		8		0.16		1		*		*		0.26		2.86	
29	0.17	0.17	10	20	0.24	2.0	3	22	0.26	2.33	0.4	4.0	0.29	0.27	2.76	2.61
30	0.022	0.14	10	16	0.20	1.9	2	23	0.04	1.14	*	0.8	0.29	0.29	2.70	2.66
31	0.36	0.13	15	47	0.36	4.2	17	170	0.55	4.48	0.5	2.4	0.30	0.35	2.42	2.80
32	0.23	1.10	9	19	0.18	0.40	6	25	0.08	0.62	*	1.0	0.31	0.31	2.38	2.40
33	0.028	0.12	9	19	0.20	5.4	13	108	0.06	1.09	*	4.2	0.31	0.30	2.43	2.66
34	0.12	0.092	13	42	0.22	2.3	6	26	0.11	1.45	*	1.8	0.29	0.29	2.34	2.78
High	1.67	2.05	45	79	1.2	5.4[c]	22	170	1.73	5.46[c]	0.8	25	0.38	0.41	7.27	7.34
Low	0.002	0.028	7	6	0.15	0.19	1	4	<0.015	0.06	<0.4	<0.4	0.08	0.08	2.06	2.11
Mean	0.12	0.45	14	24	0.28	1.4[c]	5	39	0.15	1.74	<0.4	2.0	0.29	0.29	2.69	2.94
% Rel Std Dev	240	134	61	71	87	98	114	125		87			17	23	34	37
Std Dev	0.29	0.61	8	17	0.24	1.3	6	49		1.5			0.05	0.07	0.91	1.08

a Running Sample
b Standing Sample
c Sample 23 S not included in the computation.
* Below detection limit.

TABLE 4 - ADDITIONAL DATA AND COMPARISON TO PHS STANDARDS

Sample Number	Color S[b]	Fluoride mg/l R[a]	Fluoride mg/l S	Std Plate Count /ml	Coliform /100 ml	Pseudomonas /100 ml	Mandatory S	Recommended R	Recommended S
1		0.95	0.94	3	<1	<1			Fe,Cu
2		0.05		11	<1	<1			
3		0.86		5	<1	<1			
4		0.88		1	<1	<1			
5		0.94	0.92	7	<1	<1			Fe
6		0.90	0.94	25	<1	<1		Cu	Fe,Cu
7		0.92		7	<1	<1		Fe	
8		0.90		11	<1	<1		Fe	
9		0.96		3	<1	<1			
10		0.98		1	<1	<1			
11		1.00		4	<1	<1			
12		1.00		1	<1	<1			
13	20	1.08	1.00	160	<1	<1			Fe
14		0.84	0.96	150	<1	<1			
15	Yes	0.98	1.10	700	<1	<1			Turb,Fe
16		0.10		6	<1	<1			
17		1.02	1.02	11	<1	<1			Cu
18		0.94		4	<1	<1		Fe	
19	Yes	1.00	0.98					Fe	Fe
20	20	0.96	1.06	2	<1	<1			Fe
21	45	1.00	1.00	46	<1	<1			Fe
22		1.00	0.90	3	<1	<1			Fe
23	Yes	1.00	0.96	5	<1	<1	Pb,Cd		Turb,Fe,Cu,Mn, Zn
24		1.00	0.94	45	<1	<1	Pb		Fe
25	Yes	0.92	1.25	31,000	<1	<1	Pb		Fe,Zn
26		0.96	0.98	26	<1	<1	Cd		Fe
27		0.94	0.94	330	<1	<1			Fe
28		1.00		1	<1	<1			
29	Yes	0.94	0.94	34	<1	<1			Fe
30		1.00	0.92	40	<1	<1			Fe
31	Yes	0.96	1.06	1200	<1	<1	Pb	Fe	
32		1.02	1.00	1	<1	<1			Cu
33		0.98	1.00	160	<1	<1	Pb		
34	Yes	0.54	0.94	4	<1	<1			
High		1.08	1.25	31,000					
Low		0.10	0.90	1					
Mean		0.90	0.99	1030					
% Rel Std Dev		25	7.8	520					

a Running sample
b Standing sample

TABLE 5 - NOTES AND PIPE DATA

Sample Number	Notes	Assumed Piping Material	Actual Piping Materials: Service Line Length, type, age, size	Actual Piping Materials: House Plumbing Type, age, size
1	R[a] - S[b] copper pickup	Cu[c]	75' unk[f], 8 yrs	copper,8 yr,¾"
2	Raw Tolt water - very clean			
3		Cu		
4	Some lead	Fe		
5	Mild R - S corrosion	Fe/Zn[d]	40' plastic,4 yr,3/4";18' iron 56 yr,3/4"	galv, ¾"
6	Copper high R - S, galvanized also	Cu,Fe/Zn	Copper	Copper & galv,10 yr,3/4",¾"
7	Partially standing sample? Lead, Turbid, Iron	Fe,Pb[e]		
8	" " " " " "	Fe,Pb		
9	Clean sample		2" galv	
10	" " , some copper	Cu		
11	Clean sample			
12	Clean sample			
13	Large iron, lead & zinc R-S increase	Fe/Zn,Pb	42' galv,20 yr,3/4";24' plastic,7 yr,3/4"	galv,20 yr,¾"
14	Mild increase copper, less zinc R-S; low Mg & high Ca in R&S	Cement,Cu	Mixed galv & copper service & plumbing, asbestos cement mains	
15	Large iron, zinc increase, plate count high	Fe/Zn	20' plastic, 10 yr	galv, ¾"
16	Clean sample			
17	Large R-S copper, lead increase	Cu		
18	High turbidity, some iron, partially standing?	Fe		
19	High iron, zinc, manganese in both R&S	Fe/Zn	10' copper,7 yr,3/4";490' unk 3/4"	galv,27 yr,¾"
20	Large iron, zinc pickup	Fe/Zn,Cu	18' copper,7 yr,3/4";34' unk 3/4"	galv,50 yr,¾"
21	Large iron, zinc, cadmium increase	Fe/Zn	30' iron, 60 yr, 3/4"	galv,¾"
22	" " " increase, copper in both R&S	Fe/Zn,Cu	45' galv,18 yr,3/4"	galv, 18 yr,¾"
23	Worst standing sample; not in zinc & iron averages	Fe/Zn,Cu,Pb	30' copper,9 yr,3/4";23' unk 3/4"	galv,35 yr,¾"
24	Large iron, lead, zinc increase	Fe/Zn,Pb	42' copper,12 yr,1";27 galv,12 yr,3/4"	galv,12 yr,¾"
25	Large copper, lead, zinc pick up. High plate count	Fe/Zn,Cu	42' galv,20 yr,1"; 42' unk	galv,14 yr,3/4"
26	Large iron, zinc, cadmium pickup	Fe/Zn		
27	Large zinc increase	Fe/Zn	34' galv,32 yr,3/4";30' galv,3/4"	galv,32 yr,¾"
28	Clean sample		10-15' 3/4" copper	
29	Large iron, zinc increase, copper in R&S	Fe/Zn,Cu	20' copper,23 yr,3/4";44' unk 3/4"	galv,15 yr,¾",3/4"
30	" " " "	Fe/Zn	40' steel,32 yr,3/4";25' unk 3/4"	galv,35 yr,3/4"
31	High plate count,large iron, lead, zinc increase, copper loss	Fe/Zn,Pb	44' steel,22 yr,3/4";64' unk	galv,15 yr,3/4"
32	Large copper pickup, iron, zinc increase	Cu,Fe/Zn	40' copper,3/4";39' unk	galv,40 yr,¾"
33	Large iron, lead, zinc increase	Fe/Zn	40' steel,48 yr,3/4";25' steel,¾"	unk
34	Large iron, zinc increase	Fe/Zn	20' copper,11 yr,3/4";24' galv,11 yr,3/4"	galv,11 yr,3/4"

a Running sample
b Standing sample
c Copper
d Galvanized iron
e Lead
f Unknown

TABLE 6 - MEANS AND MAXIMUMS OF RUNNING AND STANDING SAMPLES COMPARED TO RAW WATER VALUES

Parameter	Running		Standing		Raw Water
	Mean	Max.	Mean	Max.	
Temperature, °C	11	14	10	19.5	12
pH	5.8	8.9	6.1	9.1	5.4
D.O., ppm	10.3	10.8	8.2	10.3	10.6
Conductivity, µmho	22	42	25	42	18
Turbidity, FTU	0.63	2.4	3.3	28	0.45
Alkalinity, mg/l $CaCO_3$	2.5	14	4.5	14	~4
Chloride, mg/l	2.1	2.9	2.4	4.6	1.0
Fluoride, mg/l	0.90	1.08	0.99	1.25	0.05
Plate count/ml	Not sampled		1,030[a]	31,000	11
Calcium, mg/l	2.69	7.27	2.94	7.34	2.07
Magnesium, mg/l	0.29	0.38	0.29	0.41	0.33
Copper, mg/l	0.12	1.67	0.45	2.05	0.002
Iron, mg/l	0.28	1.2	1.4[b]	5.4[b]	0.17
Zinc, mg/l	0.15[c]	1.73	1.74[b]	5.46[b]	< 0.015
Cadmium, µg/l	< 0.4	0.8	2.0	25	< 0.4
Lead, µg/l	5	22	39	170	1
Manganese, µg/l	14	45	24	79	18

a The plate count mean is distorted by one high value. Only 4 plate counts were above 200/ml. The geometric mean is 14/ml.

b Sample 23-S is deleted from the mean and maximum.

c Values less than the detection limit are counted as zero.

The acid used to preserve the samples for metal determination brought the sample pH to about 2. Suspended particulate corrosion products dissolved by the acid are part of the apparent concentration. Sample 23-S was filtered before analysis because it contained a large amount of suspended corrosion products. Its extreme values were not included in the Zn and Fe means because of the possibility of the acid effect.

DISCUSSION

Average air temperature during October was close to the average running water temperature. The standing samples were warmer because the water was collected from piping systems in buildings.

Dissolved oxygen in the running samples was 95% to 100% of the saturation value. The standing average was 20% below saturation, which indicated consumption in corrosion reactions. No correlation of decreased oxygen and an increase in the corrosion products was apparent in the standing group, however.

Conductivity was slightly increased in the standing samples.

Mean turbidity increased fivefold from running to standing samples. It was a good indicator of corrosion.

pH was determined by the CO_2 equilibrium. Because the water was poorly buffered, the determination was instrumentally difficult. No significant difference existed between running and standing samples.

Mean alkalinity almost doubled from running to standing. Alkalinity increase was a good indicator of corrosion. In general, a sample set that showed an increase of 0.1 FTU and 1 mg/l alkalinity as $CaCo_3$ from running to standing, also exhibited corrosion products. Sample 30 was an exception.

The chloride concentration showed little variation. The difference between the October 12 (1 through 4, 6 through 12) and October 26 (5, 13 through 34) groups may have been caused by the residual chlorine in the earlier samples that had not yet reacted to form chloride. Instrumental error was also possible. A later check on the October 12 group showed higher values: 2-R, 1.4 mg/l; 7-R, 2.3 mg/l; and 9-R, 2.3 mg/l.

The fluoride concentration showed little variation and was close to the recommended 1.0 mg/l. The Seattle Water Department reported that the two samples with low fluoride levels were the result of temporary shutdown of the feed equipment at the treatment building.

The number of standing samples exhibiting color was indicative of the corrosion occurring in unprotected pipes. This is supported by the fact that none of the running samples, which represent water from the mains, showed color.

All samples were negative for coliform and pseudomonas. One high plate count (31,000) raised the mean to 1030 organisms/ml. With the exception of that sample, the mean was 94 organisms/ml, well below the proposed 1974 Drinking Water Standard of 500 organisms/ml. The geometric mean of all samples was 14 organisms/ml.

Calcium and magnesium levels were remarkably constant through the system and also between running and standing samples. The water did not deposit a scale.

The metals all showed increases from the raw water to the running samples with the exception of some manganese values. The increase from running to standing samples was significantly larger. Copper and galvanized iron pipe, the most common pipe materials, were vigorously attacked. Even in the worst case (Sample 23), however, the running sample contained low concentrations of corrosion products.

High manganese levels correlated well with high iron concentrations. Manganese is a constituent of iron pipes. The mean for iron increased five fold from running to standing samples. The manganese mean doubled.

Cadmium, an impurity in the zinc coating of galvanized pipes, appeared in cases of galvanized corrosion. The standing mean for cadmium was significantly above the running mean. For zinc, the mean increased over tenfold. No direct correlation between the zinc and cadmium values was established.

The copper mean increased fourfold from running to standing samples, and the lead mean increased eightfold. The source of lead was not identified, as no lead pipes were reported. Sweat-solder in copper plumbing may have been the source and could have been identified by testing sites with only solder-joined copper pipes.

Table 7 compares the corrosion-related parameters for the two types of running samples. The samples collected from reservoirs, transmission mains and pumping stations (numbers 3, 4, 7 through 12, 16, 18 and 28) are in the mains category. Those collected from buildings (numbers 1, 5, 6, 13 through 15, 17, and 19 through 27, 29 through 34) fill that category.

TABLE 7 - COMPARISON OF CORROSION PRODUCTS IN RUNNING SAMPLES TAKEN FROM MAINS AND BUILDINGS

Corrosion parameter	Mains	Buildings
Turbidity, FTU	0.88	0.52
Alkalinity, mg/l as $CACO_3$	2.2	2.1*
Cu mg/l	0.047	0.153
Pb µg/l	7.1	4.8
Fe mg/l	0.34	0.25
Mn µg/l	19	11
Zn mg/l	< 0.015	0.22
Cd µg/l	< 0.4	< 0.4

*Excluding samples 14 and 15 (see text).

Values from mains group are lower in copper and zinc than those from the buildings, but higher in turbidity, lead, iron, and manganese. Alkalinity and cadmium values are the same for both groups. The lack of uniform differences between the two types of sampling points indicates that the short sampling lines in the mains group were contributing corrosion products to the water.

Further evidence supporting the theory that the mains were not contributing corrosion products was provided by sample site 9. The sample came through a 6-inch main off a distribution main and then through a 2-inch galvanized line to a continuously running tap. The concentration of each metal in this sample was identical to the concentration found in the raw water.

The notes (Table 5) provide a quick summary of the corrosion products in each sample, including differences between the running and standing samples. "Clean" means relatively free of metals, that is, similar to the running average.

An assumption was made of the type of piping material through which the sample was drawn. The assumption is based on the corrosion products summarized in the notes.

The identification of actual piping materials proved difficult and was not completed. There are three sections of pipe between the main to the faucet.

(1) A service line from the main to the meter, which is near the sidewalk.

(2) A line from the meter to the building. This category was rarely known. When the information was available, it was included under the service line heading.

(3) Plumbing inside the building.

Where the actual pipe data were complete, correlation with assumed materials was good. Analysis of corrosion products can provide a reliable method of identifying buried pipes. Frequent mixtures of piping materials prevented the calculation of a corrosion rate for any particular metal in this distribution system.

Sample sites 14 and 15 were located in the Duvall Water District, which buys Tolt water wholesale from Seattle. Water reaching the service line of site 15 passed through 1 1/2 to 2 miles of 10-inch asbestos-cement main at a high flow rate. To reach site 14, the water passed through the same main, plus an additional 800 feet of 10-inch, 400 feet of 6-inch, and 1000 feet of 4-inch pipe, all made of asbestos-cement. Flow rates in the smaller sections were not as high as in the 10-inch main. Both sets of samples contained corrosion products from building plumbing. They also exhibited differences from the mean of all samples in parameters not directly related to the corrosion of exposed metal. These data have been summarized in Table 8.

TABLE 8 - WATER QUALITY CHANGES ATTRIBUTED TO ASBESTOS-CEMENT PIPE

Parameter	Sample 14		Sample 15		Mean of all Samples	
	R	S	R	S	R	S
pH	8.9	9.1	5.9	5.8	5.8	6.1
Alkalinity mg/l as $CACO_3$	∿ 14	∿14	4.1	6.6	2.5	4.5
Conductivity, μmho	42	42	25	28	22	25
Calcium, mg/l	7.27	7.34	3.94	3.82	2.69	2.94
Magnesium, mg/l	0.08	0.08	0.18	0.21	0.29	0.29

Because parameters in this group remained constant from running to standing samples, the changes from the mean were caused by the water reacting with asbestos-cement pipe, not building plumbing. Sample site 14, with greater exposure, showed large deviations in pH, alkalinity, conductivity, and calcium. The depressed magnesium concentration may have been caused by ion exchange on the pipe walls.

Increases in pH, alkalinity, and calcium have been observed by the Seattle Water Department in water from freshly relined mains. The water quality changes cease after a few weeks of flow, presumably after the uncombined calcium oxide has been removed from the cement. This is in contrast to asbestos-cement pipe, which is specifically manufactured to contain no uncombined calcium oxide.

COMPARISON OF SAMPLE VALUES WITH THE 1962 U.S. P.H.S. DRINKING WATER STANDARDS

Eighteen of the twenty-two standing samples exceeded one or more of the recommended limits of the 1962 P.H.S. Drinking Water Standards. Six of these also exceeded the mandatory limits. Six of the thirty-four running samples exceeded the recommended limits, but none were above the mandatory levels. On Table 9, the breakdown is by constituent.

TABLE 9 - NUMBER OF SAMPLES EXCEEDING P.H.S. DRINKING WATER STANDARDS

Parameter	Exceed mandatory limits		Exceed mandatory limits	
	Running	Standing	Running	Standing
Lead	0	5		
Cadmium	0	2		
Iron			5	16
Copper			1	5
Zinc			0	2
Manganese			0	1
Turbidity			0	2

APPENDIX

ATOMIC ABSORPTION WITH A HEATED GRAPHITE ATOMIZER

In the study of corrosion products in the Seattle drinking water distribution system, metal concentrations far below the detection limit for conventional flame atomic absorption were encountered. The normal techniques of preconcentration by boiling or extraction were rejected in favor of the graphite furnace modification of the atomic absorption method.

This technique was selected on the basis of reports in the literature (2-4) and a demonstration of the Perkin-Elmer HGA 2000. A brief review of the flameless atomic absorption technique was printed in American Laboratory in August 1972 (5). Caldwell, Yee, and McFarren [6] reported in 1974 that concentrations of chloride, sulfate and nitrate higher than the levels in Seattle tap water caused suppression of the signal in lead analyses.

A Perkin-Elmer model 303 atomic absorption spectrophotometer was fitted with an HGA 2000 Heated Graphite Analyzer. The absorbance signal from the spectrophotometer was automatically recorded on a strip chart. The peak heights were converted to concentration values from a curve fitted to a least-squares parabolic fit of the known standards.

Glassware cleaned with acid was essential to prevent contamination of samples or standards. Volumetric flasks, previously washed with detergent, were prepared for microgram-per-liter-level standards by the following procedure:

(1) 24 hours filled with 8N HNO_3, prepared with deionized water (1:1 conc HNO_3),

(2) 4 rinses with deionized water,

(3) 24 hours filled with deionized water,

(4) refilled with deionized water for storage.

The clean flasks were segregated from other laboratory glassware and were not exposed to tap water or detergents. As previously reported (7,8), rubber stoppers contaminated the standards and they were not used. Before flasks were refilled with a standard, they were rinsed with nitric acid, which had been saved from the initial washing procedure, and deionized water.

Standards were prepared fresh daily and stabilized with 0.1 ml concentrated nitric acid per 100 ml solution. Less than 5% concentration loss at the 10 ug/l level was observed after 3-days of storage. Aliquots of standards at concentrations below 10 mg/l were transferred with plastic tapped pipets (e.g., Eppendorf). After several operations, including rinses with

deionized water, tips were discarded because they failed to empty completely.

The spectrophotometer was similarly adjusted to the settings for the flame technique, with the following changes. When the hollow cathode lamp was adjusted as described in the instruction manual, a 15% increase in the photomultiplier gain from the "flame" setting was required to compensate for the reduced light intensity. When properly aligned, the furnace assembly physically blocked some of the incident light. This was measured as less than 10% absorption, versus no obstacles in the beam. The recorder was activated automatically by the temperature programming unit.

Typical operating parameters for the furnace are shown in Table 1. Drying time at 150° C was 40 seconds for 100 µl samples and 30 seconds for 25 µl and 10 µl samples.

The length of char cycle depended on the amount of organic material in the sample. If no organics were present, as in Seattle tap water, 15 seconds was allowed for the recorder to establish a baseline.

The char temperature was increased in a series of experiments to determine the highest temperature that did not result in volatilization and loss of the metal. Transition metals were charred at higher temperatures than shown in Table 10, without loss.

Absorption of the incident beam during the atomization cycle was strongly dependent on the temperature of the graphite tube. The values shown in the Table are a compromise of a number of factors that provided the best precision and accuracy.

Peak height (absorption) increased with higher temperature, but the width of the peak decreased. The temperatures chosen were low enough to permit the recorder pen to follow the signal. To prevent carry over to the next sample, the atomization temperature was high enough to volatilize the metal completely. Above 2000°C, an intense white light, which flooded the photodetector, was emitted by the graphite tube. This was avoided by lowering the atomization temperature and duration. For a 5-second atomization, the white light produced a shoulder on the side of a 50% absorption peak.

The gas interrupt function automatically stops the flow of inert gas through the graphite tube during atomization. This prolongs the time that the metal vapor is exposed to the light beam and increases the sensitivity of the method. The Table indicates where the gas interrupt was applied.

The graphite tube was heated to maximum temperature to vaporize residues between runs when assaying a low-concentration (weight) sample after a high concentration sample. It was required more often with the transition metals or when precision was poor. Prolonged loss of precision indicated the need for a new graphite tube.

TABLE 10

Typical Furnace Parameters

Metal	Char Temp.	Atomization Temp.	Atomization Time	Gas Interupt	Typical Standard	Typical Analysis µl Standard	Typical Analysis % Absorption
Cd	300°C	1800°C	6 sec.	No	10 µg/l	25 µl	40%
Co	600	2400	5				
Cr	600	2500	8	Yes	50	25	45
Cu	600	2300	6	Yes	100	25	41
Fe	600	2400	5	No	100	25	44
Mn	600	2400	5	Yes	5	100	70
	600	2400	5	No	30	25	33
Ni	600	2300	5				
Pb	600	2000	5	Yes	40	25	36
Zn	300	1300	15	No	5	25	34

When the cooling water for the furnace was below 15°C, vapor from 100-µl samples condensed on the external surfaces of the graphite cone. Some of this water vaporized or spattered during atomization, which decreased precision. The problem was eliminated by swabbing the cone with a lintless batt and heating the tube to maximum temperature after four to six samples. No condensation was observed with 10-µl or 25-µl samples.

Polyethylene tips for injecting the samples into the graphite tube were discarded after 4 to 10 samples, when graphite embedded on the outside of the tip caused wetting.

The deuterium background corrector, which eliminates interferences from broad band absorption, was not needed for the drinking water samples tested in this study.

The HGA 2000 was operated over a one-thousand fold concentration range by varying the sample volume. The time for a single analysis was longer than by flame atomic absorption. Samples were screened by the flame method, and those requiring scale explanation or noise suppression were retested with the HGA.

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